

JP 00045128A Machine Translation

【住所又は居所】宮城県仙台市青葉区川内元支倉35番地 川内住宅11-806

(72) 【発明者】

【氏名】和久 芳春

【住所又は居所】山口県宇部市大字小串1978番地の5 宇部興産株式会社宇部研究所内

(72) 【発明者】

【氏名】中川 成人

【住所又は居所】山口県宇部市大字小串1978番地の5 宇部興産株式会社宇部研究所内

(72) 【発明者】

【氏名】大坪 英樹

【住所又は居所】山口県宇部市大字小串1978番地の5 宇部興産株式会社宇部研究所内

(74) 【代理人】

【識別番号】100077517

【弁理士】

【氏名又は名称】石田 敏 (外3名)

【テーマコード(参考)】4L037

【Fターム(参考)】4L037 CS17 CS22 FA03 FA06 PA31

(57) 【要約】

【課題】 室温から高温まで引張強度が大きい無機繊維を提供すること。

【解決手段】 Ln (Lnは少なくとも一種の希土類金属元素)、A (AはAl、Cr、Fe及びGaから選ばれる少なくとも一種の元素)及びOから構成される熔融液を回転ロールに接触させて冷却し、細線状に凝固させて製造されるLn、A、及びOから構成される繊維を700~1700℃で加熱することにより製造される、結晶質のLn₃A₅O₁₂相、結晶質のLnAO₃相及び結晶質のA₂O₃相からなる群から選択される少なくとも二種の結晶質相から構成される高耐熱性無機繊維。

【Address】Miyagi Prefecture Sendai City Aoba-ku Kawauchi M ohasekura 35 Kawauchi Residence 11 - 806

(72) 【Inventor】

【Name】Kazuhisa Yoshiharu

【Address】Inside of Yamaguchi Prefecture Ube City Oaza Okus 197 8-5 Ube Industries Ltd. (DB 69-056-0008) Ube Research Laboratory

(72) 【Inventor】

【Name】Nakagawa adult

【Address】Inside of Yamaguchi Prefecture Ube City Oaza Okus 197 8-5 Ube Industries Ltd. (DB 69-056-0008) Ube Research Laboratory

(72) 【Inventor】

【Name】Otsubo Hideki

【Address】Inside of Yamaguchi Prefecture Ube City Oaza Okus 197 8-5 Ube Industries Ltd. (DB 69-056-0008) Ube Research Laboratory

(74) 【Attorney(s) Representing All Applicants】

【Applicant Code】100077517

【Patent Attorney】

【Name】ISHIDA TAKASHI (3 OTHERS)

【Theme Code (Reference)】4L037

(57) 【Abstract】

【Problem】 Offer inorganic fiber where tensile strength is large from room temperature to high temperature.

【Means of Solution】 Ln (As for Ln rare earth metal element of at least one kind), Contacting roll, it cools molten liquid which is formed from the A (As for A from Al, Cr, Fe or Ga selected from the group element of at least one kind which) and O, solidification doing in fine line, high heat resistance inorganic fiber which is formed from crystalline phase of at least two kinds which is selected from group which is produced by heating fiber which is formed from Ln, A, and O which are produced with 700 to 1700 °C, consists of crystalline Ln₃A₅O₁₂ phase, crystalline LnAO₃ phase and crystalline A₂O₃ phase.

ISTA's Paterra(tm), Version 1.5 (There may be errors in the above translation. ISTA cannot be held liable for any detriment from its use. WWW: <http://www.intlscience.com> Tel:800-430-5727)

P.2

JP 00045128A Machine Translation

【特許請求の範囲】

【請求項1】 Ln (Lnは少なくとも一種の希土類金属元素)、A (AはAl、Cr、Fe及びGaからなる群から選択される少なくとも一種の元素) 及びOから構成される溶融液を回転ロールに接触させて冷却し、繊維状に凝固させて製造されるLn、A、及びOから構成される繊維を700～1700℃で加熱することにより製造される、結晶質のLn₃A₅O₁₂相、結晶質のLnA₂O₃相及び結晶質のA₂O₃相からなる群から選択される少なくとも二種の結晶質相から構成される高耐熱性無機繊維。

【請求項2】 AがAl及び/又はCrである請求項1記載の高耐熱性無機繊維。

【請求項3】 各々の結晶質相が繊維中に均一に分散して存在し、かつその粒子径が揃っていることを特徴とする請求項1又は2記載の高耐熱性無機繊維。

【請求項4】 希土類金属元素が、Er、Yb、Dy、Y、Gd、La、Sm、Ce、Pr、Nd、Eu、Tb、Ho、Tm及びLuからなる群から選択される少なくとも一種の元素であることを特徴とする請求項1～3に記載の高耐熱性無機繊維。

【請求項5】 希土類金属元素が、Er、Yb及びDyからなる群から選択される少なくとも一種の元素であることを特徴とする請求項4に記載の高耐熱性無機繊維。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、断熱材、フィルタ材またはプラスチック、金属、セラミックス、コンクリート等の強化材等その他広範な用途に使用される無機繊維に関するものである。

【0002】

【従来の技術】 金属の弾性率及び高温強度の改善、セラミックスの靱性の改善等を目的として、Al₂O₃系、SiC系等の連続繊維をその強化材として適用するための研究開発が活発に行われている。Al₂O₃系繊維は、高温における耐酸化性が良好なことや溶融金属に対して比較的安定であることなどから、上記用途への適用が期待されている。しかしながら、Al₂O₃系繊維は、

[Claim(s)]

[Claim 1] Ln (As for Ln rare earth metal element of at least one kind), Contacting roll, it cools molten liquid which is formed from the A (As for A is selected from group which consists of the Al, Cr, Fe and Ga element of at least one kind which) and O, solidification doing in fine line, high heat resistance inorganic fiber which is formed from crystalline phase of at least two kinds which is selected from group which is produced by heating fiber which is formed from Ln, A, and O which are produced with 700 to 1700 °C, consists of crystalline Ln₃A₅O₁₂ phase, crystalline LnA₂O₃ phase and crystalline A₂O₃ phase.

[Claim 2] High heat resistance inorganic fiber which is stated in Claim 1 where A is Al and/or Cr.

[Claim 3] Each crystalline phase dispersing to uniform in fiber it exists, high heat resistance inorganic fiber which is stated in Claim 1 or 2 which designates that at same time the particle diameter has been even as feature.

[Claim 4] Rare earth metal element, high heat resistance inorganic fiber which is stated in Claim 1 to 3 which designates that it is a element of at least one kind which is selected from group which consists of Er, Yb, Dy, Y, Gd, La, Sm, Ce, Pr, Nd, Eu, Tb, Ho, Tm and Lu as feature.

[Claim 5] Rare earth metal element, high heat resistance inorganic fiber which is stated in Claim 4 which designates that it is element of at least one kind which is selected from group which consists of Er, Yb and Dy as feature.

[Description of the Invention]

【0001】

[Technological Field of Invention] This invention, is in addition something such as insulation regarding inorganic fiber which is used for broad application, filter or plastic, metal, ceramic and concrete or other reinforcement.

【0002】

[Prior Art] With modulus of metal and improvement of high temperature strength and the improvement etc of toughness of ceramic as object, Al₂O₃ system, the research and development in order to apply SiC or other continuous fiber as reinforcement is done actively. As for Al₂O₃ fiber, fact that etc it is a stability relatively from fact that oxidation resistance in high temperature is satisfactory and vis-a-vis molten metal,

ISTA's Paterra(tm), Version 1.5 (There may be errors in the above translation. ISTA cannot be held liable for any detriment from its use. WWW: <http://www.intlscience.com> Tel:800-430-5727)

P.3

JP 00045128A Machine Translation

例えば1200℃以上の温度においてその強度が低下するなど、セラミックス強化用としては耐熱性が十分に高くない。したがって、高温における耐酸化性が良好な酸化物であって、 Al_2O_3 系繊維以上の高耐熱性を有する繊維の開発が待たれている。

[0003] 米国特許第5,605,870号には、10poises以下の粘度を有する溶融液より製造されるセラミックファイバーが開示されている。この繊維は、それ自体公知のいわゆる melt extraction法により製造され、非晶質相及び/又は結晶相から構成されている。しかし、クレーム1の記載によると、「結晶粒径がlinearly surfaced line より放射線状に増加する」との限定があり、本発明による各々の結晶質相が繊維中に均一分散して存在し、かつその粒子径が揃っている無機繊維とは異なるものである。

[0004]

【発明が解決しようとする課題】上記のような現状を鑑みて、本発明者は、室温においても高温においても高強度を有し、高温における耐酸化性が良好な酸化物繊維を得べく鋭意研究を重ね、本発明に記す新規な無機繊維を見出した。すなわち、Ln (Lnは少なくとも一種の希土類金属元素)、A (AはAl、Cr、Fe及びGaからなる群から選択される少なくとも一種の元素)及びOから構成される溶融液を回転ロールに接触させて冷却し、繊維状に凝固させて製造されるLn、A、及びOから構成される繊維を700～1700℃で加熱することにより製造される、結晶質のLn₃A₅O₁₂相、結晶質のLnA₂O₃相及び結晶質のA₂O₃相からなる群から選択される少なくとも二種の結晶質相から構成される無機繊維が、室温においても高温においても高強度を有することが見出された。

[0005] 本発明の目的は、室温から高温までの引張強度が大きく、断熱材、フィルタ材またはプラスチック、金属、セラミックス、コンクリート等の強化材等その他広範な用途に好適に使用することができる無機繊維を提供することにある。

[0006]

【課題を解決するための手段】以下、本発明について詳細に説明する。本発明は、結晶質のLn₃A₅O₁₂相 (Lnは少なくとも一種の希土類金属元素、AはAl、Cr、Fe及びGaからなる群から選択される少なくとも

application to above-mentioned application is expected. But, strength heat resistance is not high in fully it decreases such as, as ceramic reinforcement as for Al_2O_3 fiber, in temperature of for example 1200 °C or higher. Therefore, being an oxide where oxidation resistance in high temperature is satisfactory, development of fiber which possesses high heat resistance above Al_2O_3 fiber is expected.

[0003] In U. S. Patent No. 5,605,870 number, ceramic fiber which is produced is disclosed from the molten liquid which possess viscosity of 10 poise s or less. This fiber is produced by so-called melt extraction method of that itself public knowledge, is constituted from amorphous phase and/or crystal phase. But, according to statement of claim 1, "crystal grain diameter from linear surface line increases in radiating wires" with this limitation, each crystalline phase which is by this invention dispersing to uniform in fiber, it exists, inorganic fiber where at same time particle diameter has been even is something which differs.

[0004]

[Problems to be Solved by the Invention] As description above considering present state, in order that these inventor has high strength regarding room temperature, and regarding high temperature obtains the oxide fiber where oxidation resistance in high temperature is satisfactory, diligent research was repeated, novel inorganic fiber which is inscribed to this invention was discovered. namely, Ln (As for Ln rare earth metal element of at least one kind), Contacting roll, it cools molten liquid which is formed from the A (As for A is selected from group which consists of the Al, Cr, Fe and Ga element of at least one kind which) and O, solidification doing in fine line, it is produced Ln, inorganic fiber which is formed from crystalline phase of at least two kinds which is selected from group which is produced by heating fiber being formed from A, and O with 700 to 1700 °C, consists of crystalline Ln₃A₅O₁₂ phase, crystalline LnA₂O₃

high strength regarding room temperature and regarding high temperature.

[0005] As for objective of this invention, tensile strength to high temperature is large from the room temperature, it is in addition such as insulation to offer inorganic fiber which can be used for ideal in broad application, filter or plastic, metal, ceramic and concrete or other reinforcement.

[0006]

[Means to Solve the Problems] You explain in detail below, concerning this invention. this invention crystalline Ln₃A₅O₁₂ phase (As for Ln rare earth metal element of at least one kind, as for A is selected from group which consists of Al, Cr,

JP 00045128A Machine Translation

一種の元素)、結晶質のLnA₂O₃相及び結晶質のA₂O₃相からなる群から選択される少なくとも二種の結晶質相から構成され、室温から1200℃の温度範囲で高い強度を有する無機繊維に関する。

[0007] この無機繊維は、Ln (Lnは少なくとも一種の希土類金属元素)、A (AはAl, Cr, Fe及びGaからなる群から選択される少なくとも一種の元素) 及びOから構成される溶融液を回転ロールに接触させて冷却し、細線状に凝固させて製造されるLn、A、及びOから構成される繊維を700～1700℃で加熱することにより製造されるものである。ここで、「結晶質」とは、透過電子顕微鏡観察によって結晶格子像を確認することができる相の原子構造を意味する。

[0008]

[発明の実施の形態] 本発明におけるLnとしては、Er, Yb, Dy, Y, Gd, La, Sm, Ce, Pr, Nd, Eu, Tb, Ho, Tm及びLuからなる群から選択される少なくとも一種の希土類金属元素が挙げられ、特に、Er, Yb, Dyは得られる無機繊維の強度が高くなるので好ましい。

[0009] Aとしては、Al, Cr, Fe及びGaからなる群から選択される少なくとも一種の元素が挙げられ、特に、AがAl及び/又はCrの場合は得られる無機繊維の高温強度が高くなるので好ましい。

[0010] 本発明の無機繊維におけるAの割合は、A₂O₃換算で10～90モル%の範囲にあることが好ましい。本発明の無機繊維は、Ln₃A₅O₁₂, LnAO₃, A₂O₃で表わされる結晶相の群から選ばれた少なくとも二種の結晶相 (例えばAl₂O₃でもAが異なれば異なる結晶相) で構成される実質的に結晶質相のみよりなるものであるが、結晶粒界には非晶質相が存在し得る。また、本発明の無機繊維の形状は、特に限定されないが、円形又は円形に近い断面を有することが好ましい。本発明の無機繊維は連続繊維としても短繊維としても使用できる。無機繊維の横断面の寸法は、断面形状にもより一重ではないが、3～50μmの直径を有するものが良く、5～30μmの直径を有するものがより好ましい。

[0011] 本発明の無機繊維の室温、好ましくはさらに1200℃における引張強度は、1.6GPa以上、好

Fe and Ga element of the at least one kind which), is formed from crystalline phase of at least two kinds which is selected from group which consists of crystalline LnA₂O₃ phase and crystalline A₂O₃ phase regards inorganic fiber which from room temperature possesses high strength with temperature range of 1200 °C.

[0007] It is something which is produced by heating fiber which is formed from Ln, A, and O where this inorganic fiber, the Ln (As for Ln rare earth metal element of at least one kind), contacting roll, cools molten liquid which is formed from A (As for A is selected from group which consists of the Al, Cr, Fe and Ga element of at least one kind which) and O, solidification does in fine line and is produced with 700 to 1700 °C. Here, "crystalline" with, atom construction of phase which can verify crystal lattice image by transmission electron microscope observation is meant.

[0008]

[Embodiment of Invention] Be able to list rare earth metal element of at least one kind which is selected from the group which consists of Er, Yb, Dy, Y, Gd, La, Sm, Ce, Pr, Nd, Eu, Tb, Ho, Tm and Lu as Ln in the this invention, because especially, as for Er, Yb, Dy strength of inorganic fiber which is acquired becomes high, it is desirable.

[0009] As A, be able to list element of at least one kind which is selected from group which consists of Al, Cr, Fe and Ga, when especially, A is Al and/or Cr, because high temperature strength of inorganic fiber which is acquired becomes high it is desirable.

[0010] As for ratio of A in inorganic fiber of this invention, it is desirable with A₂O₃ conversion to be range of 10 to 90 mole%. inorganic fiber of this invention is constituted is something which consists of only crystalline phase substantially with crystal phase (If A differs even in for example A₂O₃, it differs crystal phase) of at least two kinds which is chosen from group of crystal phase which is displayed with Ln₃A₅O₁₂, LnAO₃, A₂O₃, but amorphous phase can exist in crystal grain boundary. In addition, shape of inorganic fiber of this invention is not limited especially. It is desirable to possess cross section which is close to round or the round. As continuous fiber also as short fiber you can use inorganic fiber of this invention. dimension of cross-section of inorganic fiber is not more one approximation even in cross section shape. Those which possess diameter of 3 to 50 μm are good, those which possess diameter of 5 to 30 μm are more desirable.

[0011] Room temperature of inorganic fiber of this invention, preferably furthermore as for the tensile strength in 1200 °C,

ISTA's Paterra(tm), Version 1.5 (There may be errors in the above translation. ISTA cannot be held liable for any detriment from its use. WWW: <http://www.intlscience.com> Tel:800-430-5727)

P.5

JP 00045128A Machine Translation

ましくは2.0GPa以上であることが望ましい。本発明の無機繊維は、高い強度を有し、室温より1200℃までの温度範囲ではその強度はほとんど温度依存性を示さないことから、例えば、セラミックスの強化用繊維や高温炉の断熱材等として特に有用である。

【0012】本発明の無機繊維は、Ln、A及びOから構成される溶融液を回転ロールに接触させて冷却し、細線状に凝固させて製造されるLn、A、及びOから構成される繊維を700～1700℃で加熱することにより製造される。700～1700℃での加熱前の繊維（以下、中間繊維と記す）は、特開平9-353270号に記載された方法によって製造される。以下、その方法について詳細に説明する。

【0013】溶融前の原料としては、一般的にはLnの酸化物及びAの酸化物が用いられるが、溶融したときに酸化物になるものであれば良く、水酸化物、炭酸塩等を用いても良い。原料の形態としては、粉体、成形体、焼結体、凝団体のいずれでも良く、また、これらの二つ以上が組み合わさったものでも良い。

【0014】前記の原料の溶融方法は、少なくとも該原料の回転ロールに接触する部分をその融点以上の温度に加熱することが可能な方法であればいかなる方法でも良く、加熱源として、例えば、アーク、レーザー、電子ビーム、光、赤外線、高周波等を用いることができる。高周波を用いる場合は、該原料が室温近傍においてほとんど導電性を有さないために、導電性を有しかつ該原料の融点より高い融点を有する増塊に該原料を収容する必要がある。例えば、Mo、W、Ta、Ir、Nb等の増塊が好適に用いられる。また、原料が粉体である場合も上記のような材質の増塊や支持台を用いる必要があるが、この場合は上記増塊に加えて、水などによって冷却を施したCu製の増塊や支持台等を使用することもできる。原料が粉体である場合以外でもこれらの増塊や支持台等を好適に使用することができる。

【0015】原料の溶解は、大気中、不活性ガス中、還元性ガス中、炭化水素ガス中、真空中などいかなる雰囲気中で行われても良いが、原料の融点以下の温度において酸化されやすい増塊等を用いる場合は、アルゴンガスやヘリウムガスなどの不活性ガス雰囲気中または真空中などで溶解を行うことが好ましい。また、アークにより

it is desirable to be a 1.5 GPa or greater and a preferably 2.0 GPa or greater. inorganic fiber of this invention has high strength, with temperature range to 1200 °C as for strength especially it is useful from room temperature from fact that for most part temperature dependence is not shown, as reinforcement fiber of the for example ceramic and insulation etc of high temperature furnace.

[0012] Inorganic fiber of this invention, contacting roll, cools molten liquid which is formed from Ln, A and O, clotting does in the fine line and is produced by heating fiber which is formed from the Ln, A, and O which are produced with the 700 to 1700 °C. fiber (Below, intermediate filament you inscribe.) before heating with 700 to 1700 °C is produced by method which is stated in Japan Patent Application Hei 9 - 353270 number. You explain in detail below, concerning method.

[0013] As starting material before melting, generally it can use oxide of the Ln and oxide of A, but when melting, if it is something which becomes oxide, to be good, making use of hydroxide and carbonate etc it is good. As form of starting material, it is good with whichever of powder, the molded article, sinter and coagulant, in addition, these two or more unite and are good being something which is brought together.

[0014] If dissolving method of aforementioned starting material is method whose it is possible to heat portion which at least contacts roll of the said starting material to temperature of melting point or higher, it is good any method, it can use for example arc, laser, electron beam, light, infrared light and high frequency etc as the heat source. When high frequency is used, said starting material because for most part it does not possess electrical conductivity in room temperature vicinity, electrical conductivity it is necessary to accommodate said starting material in crucible which possesses high melting point from the melting point of possessing and said starting material. It can use for ideal for example Mo, W, Ta, Ir, Nb or other crucible. In addition, when starting material is powder, a description above the crucible of material and it is necessary to use support table, but in this case it can also use crucible and support table etc of Cu which administers cooling in addition to above-mentioned crucible, with water etc. When starting material is powder, these crucible and support table etc can be used for ideal at in addition to.

[0015] Melting starting material is good being done, in atmosphere, in inert gas, in the reductive gas, in hydrocarbon gas and in vacuum middle class whatever atmosphere, but when crucible etc which oxidation is easy to be done is used in the temperature of melting point or lower of starting material, it is desirable to melt at in or vacuum middle class argon gas and helium gas or

JP 00045128A Machine Translation

原料を溶解する場合は、アークが発生するに十分なアルゴンガス等が雰囲気中に含まれている必要がある。

【0016】回転ロールの材質には特に制限はないが、熱伝導率が高いものや高融点金属などがロールの寿命や得られる繊維の品質の安定性の点で好ましい。具体的には、Cu、Cu合金、Mo、Ta、W、Ir等を好適に使用することができる。回転ロールと熔融液との接触は、例えば、熔融液に回転ロールの先端を回転接触させる、あるいは回転ロール上に熔融液を落下させるなどのいずれの態様でも良い。ただし、回転ロールの形状としては、その先端が熔融液と小さい面積で接触することが可能なものが、得られる繊維の断面形状を均一にするのに都合が良く、例えば図1に示すように、先端にV字型の突起を有する回転ロールを好適に使用することができる。

【0017】このような回転ロールを熔融液に接触させる際の回転ロールの周速度は10m/sec以下であることが望ましい。周速度が10m/secより速い場合は、断面積が一定の繊維を得ることが難しくなる場合があるためである。

【0018】本発明の中間繊維を製造する装置としては、例えば図2に示すような機構を有するものを使用することができる。W電極(1)と水冷を施されたCu製坩堝(2)の間に発生させたアーク(3)により溶解されたLn、A及びOから構成される熔融液(4)をCu製坩堝を横方向に移動させることにより矢印の方向に回転するロール(5)に接触させ、繊維状に凝固させることで上記元素より構成される中間繊維(6)を得るものである。

【0019】中間繊維から本発明の無機繊維への転換は、中間繊維を700~1700℃で加熱することにより行われる。熱処理の温度、時間、昇降温度等を適宜選択することにより目的とする無機繊維を得ることができる。中間繊維の加熱方法は、該繊維を700~1700℃に加熱することが可能な方法であればいかなる方法でも良く、加熱源として、例えば、通電により発熱するSiC、MoSi₂などの発熱体、高周波、レーザー、電子ビーム、光、赤外線等を用いることができる。

【0020】一般的には、Al₂O₃、SiC等のセラミックス、Mo、Ta、W、Ir、Nb等の高融点金属製の坩堝等に中間繊維を収容して、坩堝ごと加熱を行う、または、同様の素材からなるドラムに中間繊維を巻き取り、ドラムごと加熱を行うなどの方法が用いられる。

other inert gas atmosphere. In addition, when starting material is melted with arc, arc occurs has necessity for sufficient argon gas etc to be included in atmosphere.

【0016】There is not especially restriction in material of roll. Thermal conductivity is large are desirable in the lifetime of roll and point of stability of quality of the fiber which is acquired. Concretely, Cu, Cu alloy and Mo, Ta, W, Ir etc can be used for ideal. Contact with roll and molten liquid end of roll turns contacts for example molten liquid, or it is good or other any embodiment which molten liquid falls on roll. However, as end molten liquid those whose it is possible with the small surface area to contact, are convenient in order to designate the cross section shape of fiber which is acquired as uniform as shape of the roll, shown in for example Figure 1, roll which possesses protrusion of the V-shape in end can be used for ideal.

【0017】This kind of roll case where it contacts molten liquid as or the perimeter velocity of roll it is desirable to be below 10 m/sec. When perimeter velocity is faster than 10 m/sec, is because there are times when it becomes difficult for cross-sectional area to obtain fixed fiber.

【0018】Those which possess kind of mechanism which is shown in for example Figure 2 as the equipment which produces intermediate filament of this invention, can be used. It was melted by arc (3) which occurs between Cu make crucible (2) which is administered W electrode (1) and water cooling Ln, Contacting roll (5) which turns to direction of arrow molten liquid (4) being formed from A and O by moving Cu make crucible to transverse direction, it is something which obtains intermediate filament (6) which from the above-mentioned element consists of thing which solidification is done in fine line.

【0019】Conversion to inorganic fiber of this invention is done from intermediate filament by heating the intermediate filament with 700 to 1700 °C. inorganic fiber which is made objective temperature of thermal processing, by selecting time and heating and cooling rate etc appropriately can be acquired. If heating method of intermediate filament is method whose it is possible to heat the said fiber to 700 to 1700 °C, it is good any method, it can use SiC, MoSi₂ or other heat emitter, the high frequency, laser, electron beam, light and infrared light etc which the heat emission arc done as heat source, with for example electrification.

【0020】Generally, accommodating intermediate filament in Al₂O₃, SiC or other ceramic and crucible etc of the Mo, Ta, W, Ir, Nb or other high melting point metallic, every crucible it heats, or, every windup and drum or other method which heats can use intermediate filament for drum which consists of the similar

JP 00045128A Machine Translation

他にも、所定の温度に昇温された管状炉の炉内に繊維を連続して通す方法などを適用することもできる。また、より高い強度を有する繊維を得るためには、繊維が繊維方向に成長するように、中間繊維が繊維の片側から繊維方向に徐々に加熱を受けるような方向加熱を行うこともできる。この場合の加熱処理は、上述のような管状炉の炉内に繊維を連続して通す方法によっても可能であるが、レーザー、電子ビーム、光、赤外線等を用いて、繊維又は被加熱部を繊維方向に移動させる方法を適用することもできる。

【0021】中間繊維の加熱処理は、大気中、不活性ガス中、還元性ガス中、炭化水素ガス中、真空中などいかなる雰囲気中で行われても良いが、用いられる坩堝、ドラム等の材質により制限を受ける場合がある。

【0022】

【実施例】以下、実施例及び比較例を示して本発明についてさらに具体的に説明する。

実施例 1

原料には α - Al_2O_3 粉末と Er_2O_3 粉末を用いた。 α - Al_2O_3 粉末と Er_2O_3 粉末をモル比で前者を81.1、後者を18.9の割合でエタノールを用いた湿式ボールミルによって混合し、得られたスラリーからロータリーエバポレータを用いてエタノールを除去した。得られた混合粉末をステンレス製のダイスを用いて一軸プレスにより直径10mm、高さ10mmの円柱状に成形し、次いでこの円柱状成形体をアークにより溶解しボタン状の凝固体を得た。このボタン状凝固体を図2に示す水冷を施したCu製坩堝(2)に収容し、その後、図2の機構が収容される系内を-0.04MPaのアルゴンガス雰囲気にし、W電極とCu製坩堝の間にアークを発生させた。アークによってボタン状凝固体を溶解し、この溶解状態を維持したまま、Cu製坩堝を移動させて、2m/secの周速度で回転する先端に30°のV字型突起を有する直径70mmのCu製ロールに接触させ、平均直径15 μm の連続繊維を得た。次いで、この中間繊維を Al_2O_3 製の坩堝に収容し、 MoSi_2 製の発熱体が装着された箱型の電気炉を用いて空気中で加熱処理を行った。1000°C/hrの速度で昇温し、1400°Cで2hr保持した後に降温し、平均直径14 μm の連続繊維を得た。得られた繊維は、Cu-K α 線を用いたX線回折及び走査電子顕微鏡観察により、複数の100~150nmの $\text{Er}_3\text{Al}_5\text{O}_{12}$ 相及び複数の100~150nmの

material. In specified temperature continuing fiber inside furnace of tube furnace which the temperature rise is done is possible also fact that it applies method etc which it passes to in addition to. In addition, in order to obtain fiber which possesses a higher strength, in order for crystal to grow in fiber direction, it is possible also to do one direction kind of heating where intermediate filament from the one side of fiber gradually receives heating to fiber direction. It is possible also to apply method which moves fiber or suffering heated part to fiber direction as for heat treatment in this case, continuing fiber inside furnace of tube furnace, an above-mentioned way it is possible but, making use of laser, electron beam, light and the infrared light etc with method which it passes.

【0021】 Heat treatment of intermediate filament is good being done, in atmosphere, in inert gas, in reductive gas, in hydrocarbon gas and in vacuum middle class whatever atmosphere, but there are times when restriction is received with crucible and drum or other material which are used.

【0022】

【Working Example(s)] Below, showing Working Example and Comparative Example, furthermore you explain concretely concerning this invention.

Working Example 1

- Al_2O_3 powder and Er_2O_3 powder were used to starting material. - Al_2O_3 powder and Er_2O_3 powder former 81.1 and the latter were mixed with mole ratio with wet ball mill which uses ethanol at ratio of the 18.9, ethanol was removed making use of rotary evaporator from the slurry which is acquired. mixed powder which is acquired making use of die of the stainless steel it formed in cylinder of diameter 10 mm and height 10 mm with the single screw press, next it melted this cylinder molded article with arc and acquired coagulant of button. It accommodated in Cu make crucible (2) which administers water cooling which shows this button coagulant in Figure 2 after the designated inside of system where mechanism of Figure 2 is accommodated as the argon gas atmosphere of -0.04 MPa, generated arc between W electrode and the Cu make crucible. I melted button coagulant with arc, while this dissolved state is maintained, moving Cu make crucible, contacting Cu make roll of the diameter 70 mm which possesses V-shape protuberance of 30° in end which turns with perimeter velocity of 2 m/sec, it acquired continuous fiber of average diameter 15 μm . Next, this intermediate filament was accommodated in crucible of Al_2O_3 make, the heat treatment was done in air making use of electric furnace of box shape where the heat emitter of MoSi_2 make is mounted. temperature rise it did with rate of 1000 °C/hr, 2 hr after keeping, the cooling it did with 1400 °C,

ISTA's Paterra(tm), Version 1.5 (There may be errors in the above translation. ISTA cannot be held liable for any detriment from its use. WWW: <http://www.intlscience.com> Tel:800-430-5727)

P.8

JP 00045128A Machine Translation

の Al_2O_3 相から構成された結晶質であり、各々の結晶相が繊維中に均一に分散して存在していることがわかった。また、この繊維の引張試験を、室温の場合は負荷速度 2mm/min 、スパン 25mm の条件で、 1000°C 及び 1200°C の空気中の場合は負荷速度 2mm/min 、スパン 100mm の条件で行った。測定された室温、 1000°C 及び 1200°C での引張強度の平均値を表 1 に示す。

【0023】実施例 2

原料に $\alpha\text{-Al}_2\text{O}_3$ 粉末と Yb_2O_3 粉末を用い、その割合をモル比で前者を 83.7、後者を 16.3 とした以外は実施例 1 と同様の方法で連続繊維を得た。得られた繊維は実施例 1 と同様の分析により、複数の $100\sim 150\text{nm}$ の $\text{Yb}_3\text{Al}_5\text{O}_{12}$ 相及び複数の $100\sim 150\text{nm}$ の Al_2O_3 相から構成された結晶質であり、各々の結晶相が繊維中に均一に分散して存在していることがわかった。また、この繊維の引張試験を実施例 1 と同様にして行った結果を表 1 に示す。

【0024】実施例 3

原料に $\alpha\text{-Al}_2\text{O}_3$ 粉末と Dy_2O_3 粉末を用い、その割合をモル比で前者を 78.9、後者を 21.1 とした以外は実施例 1 と同様の方法で連続繊維を得た。得られた繊維は実施例 1 と同様の分析により、複数の $100\sim 150\text{nm}$ の $\text{Dy}_3\text{Al}_5\text{O}_{12}$ 相及び複数の $100\sim 150\text{nm}$ の Al_2O_3 相から構成された結晶質であり、各々の結晶相が繊維中に均一に分散して存在していることがわかった。また、この繊維の引張試験を実施例 1 と同様にして行った結果を表 1 に示す。

【0025】実施例 4

原料に $\alpha\text{-Al}_2\text{O}_3$ 粉末と Y_2O_3 粉末を用い、その割合をモル比で前者を 82、後者を 18 とした以外は実施例 1 と同様の方法で連続繊維を得た。得られた繊維は実施例 1 と同様の分析により、複数の $150\sim 200\text{nm}$ の $\text{Y}_3\text{Al}_5\text{O}_{12}$ 相及び複数の $150\sim 200\text{nm}$ の Al_2O_3 相から構成された結晶質であり、各々の結晶相が

acquired continuous fiber of average diameter $14\ \mu\text{m}$ fiber which is acquired, it was a crystalline which is formed from $\text{Er}_3\text{Al}_5\text{O}_{12}$ phase of 100 to 150nm of plural and Al_2O_3 phase of the 100 to 150nm of plural by X-ray diffraction and scanning electron microscope observation which use the CuK α -line, each crystal phase dispersed to uniform in fiber and it understood that it exists. In addition, tensile test of this fiber, in case of room temperature when with the condition of load rate 2mm/min and span 25mm , it is in air of 1000°C and 1200°C , it did with condition of load rate 2mm/min and span 100mm . mean value of tensile strength with room temperature, 1000°C and 1200°C which were measured is shown in Table 1.

[0023] Working Example 2

In starting material proportion with mole ratio former other than designating the 83.7 and the latter as 16.3, continuous fiber was acquired with the method which is similar to Working Example 1 making use of Al_2O_3 powder and the Yb_2O_3 powder. fiber which is acquired was crystalline which is formed from $\text{Yb}_3\text{Al}_5\text{O}_{12}$ phase of 100 to 150nm of multiple and Al_2O_3 phase of the 100 to 150nm of multiple by analysis which is similar to Working Example 1, each crystal phase dispersed to uniform in fiber and it understood that it exists. In addition, result of doing tensile test of this fiber in same way as Working Example 1 is shown in Table 1.

[0024] Working Example 3

In starting material proportion with mole ratio former other than designating the 78.9 and the latter as 21.1, continuous fiber was acquired with the method which is similar to Working Example 1 making use of Al_2O_3 powder and the Dy_2O_3 powder. fiber which is acquired was crystalline which is formed from $\text{Dy}_3\text{Al}_5\text{O}_{12}$ phase of 100 to 150nm of multiple and Al_2O_3 phase of the 100 to 150nm of multiple by analysis which is similar to Working Example 1, each crystal phase dispersed to uniform in fiber and it understood that it exists. In addition, result of doing tensile test of this fiber in same way as Working Example 1 is shown in Table 1.

[0025] Working Example 4

In starting material proportion with mole ratio former other than designating the 82 and the latter as 18, continuous fiber was acquired with the method which is similar to Working Example 1 making use of Al_2O_3 powder and the Y_2O_3 powder. fiber which is acquired was crystalline which is formed from $\text{Y}_3\text{Al}_5\text{O}_{12}$ phase of 150 to 200nm of multiple and Al_2O_3

JP 00045128A Machine Translation

繊維中に均一に分散して存在していることがわかった。また、この繊維の引張試験を実施例 1 と同様にして行った結果を表 1 に示す。

【0026】実施例 6

原料に α - Al_2O_3 粉末と Gd_2O_3 粉末を用い、その混合比をモル比で前者を 78、後者を 22 とし、中間繊維の加熱処理温度を 1300°C とした以外は実施例 1 と同様の方法で連続繊維を得た。得られた繊維は実施例 1 と同様の分析により、複数の 120~160 nm の GdAlO_3 相及び複数の 120~160 nm の Al_2O_3 相から構成された結晶質であり、各々の結晶相が繊維中に均一に分散して存在していることがわかった。また、この繊維の引張試験を実施例 1 と同様にして行った結果を表 1 に示す。

【0027】実施例 6

原料に α - Al_2O_3 粉末と Sm_2O_3 粉末を用い、その混合比をモル比で前者を 89、後者を 31 とした以外は実施例 1 と同様の方法で連続繊維を得た。得られた繊維は実施例 1 と同様の分析により、複数の 120~160 nm の SmAlO_3 相及び複数の 120~160 nm の Al_2O_3 相から構成された結晶質であり、各々の結晶相が繊維中に均一に分散して存在していることがわかった。また、この繊維の引張試験を実施例 1 と同様にして行った結果を表 1 に示す。

【0028】実施例 7

原料に α - Al_2O_3 粉末と La_2O_3 粉末を用い、その混合比をモル比で前者を 77.5、後者を 22.5 とし、また回転ロールの周速度を 1 m/sec にした以外は実施例 1 と同様の方法で連続繊維を得た。得られた繊維は実施例 1 と同様の分析により、複数の 120~160 nm の LaAlO_3 相及び複数の 120~160 nm の Al_2O_3 相から構成された結晶質であり、各々の結晶相が繊維中に均一に分散して存在していることがわかった。また、この繊維の引張試験を実施例 1 と同様にして行った結果を表 1 に示す。

【0029】実施例 8

phase of the 150 to 200 nm of multiple by analysis which is similar to Working Example 1, each crystal phase dispersed to uniform in fiber and it understood that it exists. In addition, result of doing tensile test of this fiber in sameway as Working Example 1 is shown in Table 1.

【0026】Working Example 5

In starting material proportion former 78 and the latter were designated as 22 with mole ratio making use of α - Al_2O_3 powder and the Gd_2O_3 powder, other than designating heat treatment temperature of intermediate filament as 1300 °C, the continuous fiber was acquired with method which is similar to Working Example 1. fiber which is acquired was crystalline which is formed from GdAlO_3 phase of 120 to 160 nm of multiple and Al_2O_3 phase of the 120 to 160 nm of multiple by analysis which is similar to Working Example 1, each crystal phase dispersed to uniform in fiber and it understood that it exists. In addition, result of doing tensile test of this fiber in sameway as Working Example 1 is shown in Table 1.

【0027】Working Example 6

In starting material proportion with mole ratio former other than designating the 69 and the latter as 31, continuous fiber was acquired with the method which is similar to Working Example 1 making use of α - Al_2O_3 powder and the Sm_2O_3 powder. fiber which is acquired was crystalline which is formed from SmAlO_3 phase of 120 to 160 nm of multiple and Al_2O_3 phase of the 120 to 160 nm of multiple by analysis which is similar to Working Example 1, each crystal phase dispersed to uniform in fiber and it understood that it exists. In addition, result of doing tensile test of this fiber in sameway as Working Example 1 is shown in Table 1.

【0028】Working Example 7

In starting material proportion former 77.5 and the latter were designated as 22.5 with mole ratio making use of α - Al_2O_3 powder and the La_2O_3 powder, in addition other than designating perimeter velocity of roll as the 1 m/sec, continuous fiber was acquired with method which is similar to Working Example 5. fiber which is acquired was crystalline which is formed from LaAlO_3 phase of 120 to 160 nm of plural and Al_2O_3 phase of the 120 to 160 nm of plural by analysis which is similar to Working Example 1, each crystal phase dispersed to uniform in fiber and it understood that it exists. In addition, result of doing tensile test of this fiber in sameway as Working Example 1 is shown in Table 1.

【0029】Working Example 8

ISTA's Paterra(tm), Version 1.5 (There may be errors in the above translation. ISTA cannot be held liable for any detriment from its use. WWW: <http://www.intlscience.com> Tel:800-430-5727)

P.10

JP 00045128A Machine Translation

原料に Cr_2O_3 粉末と Er_2O_3 粉末を用い、その混合比をモル比で前者を78、後者を22とした以外は実施例1と同様の方法で連続繊維を得た。得られた繊維は実施例1と同様の分析により、複数の150~200nmの ErCrO_3 相及び複数の150~200nmの Cr_2O_3 相から構成された結晶質であり、各々の結晶相が繊維中に均一に分散して存在していることがわかった。また、この繊維の引張試験を実施例1と同様に行った結果を表1に示す。

【0030】 実施例9

原料に Cr_2O_3 粉末と Gd_2O_3 粉末を用い、その混合比をモル比で前者を80、後者を20とした以外は実施例1と同様の方法で連続繊維を得た。得られた繊維は実施例1と同様の分析により、複数の150~200nmの GdCrO_3 相及び複数の150~200nmの Cr_2O_3 相から構成された結晶質であり、各々の結晶相が繊維中に均一に分散して存在していることがわかった。また、この繊維の引張試験を実施例1と同様に行った結果を表1に示す。

【0031】 実施例10

原料に Ga_2O_3 粉末と Gd_2O_3 粉末を用い、その混合比をモル比で前者を69.2、後者を30.8とした以外は実施例1と同様の方法で連続繊維を得た。得られた繊維は実施例1と同様の分析により、複数の150~200nmの $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ 相及び複数の150~200nmの Ga_2O_3 相から構成された結晶質であり、各々の結晶相が繊維中に均一に分散して存在していることがわかった。また、この繊維の引張試験を実施例1と同様に行った結果を表1に示す。

【0032】 比較例1

原料に $\alpha\text{-Al}_2\text{O}_3$ 粉末と ZrO_2 粉末を用い、その混合比をモル比で前者を62、後者を38とし、また回転ロールの周速度を0.5m/sec にした以外は実施例1と同様の方法で連続繊維を得た。得られた繊維は実施例1と同様の分析により、複数の100~1500nmの ZrO_2 相、複数の100~1000nmの Al_2O_3 相から構成されており、相対的に粗大な結晶相がロールの接触部分から放射線状に成長していることがわかった。

In starting material proportion with mole ratio former other than designating the 78 and the latter as 22, continuous fiber was acquired with the method which is similar to Working Example making use of Cr_2O_3 powder and the Er_2O_3 powder. fiber which is acquired was crystalline which is formed from ErCrO_3 phase of 150 to 200 nm of multiple and Cr_2O_3 phase of the 150 to 200 nm of multiple by analysis which is similar to Working Example 1, each crystal phase dispersed to uniform in fiber and it understood that it exists. In addition, result of doing tensile test of this fiber in sameway as Working Example 1 is shown in Table 1.

[0030] Working Example 9

In starting material proportion with mole ratio former other than designating the 80 and the latter as 20, continuous fiber was acquired with the method which is similar to Working Example making use of Cr_2O_3 powder and the Gd_2O_3 powder. fiber which is acquired was crystalline which is formed from GdCrO_3 phase of 150 to 200 nm of multiple and Cr_2O_3 phase of the 150 to 200 nm of multiple by analysis which is similar to Working Example 1, each crystal phase dispersed to uniform in fiber and it understood that it exists. In addition, result of doing tensile test of this fiber in sameway as Working Example 1 is shown in Table 1.

[0031] Working Example 10

In starting material proportion with mole ratio former other than designating the 69.2 and the latter as 30.8, continuous fiber was acquired with the method which is similar to Working Example 1 making use of Ga_2O_3 powder and the Gd_2O_3 powder. fiber which is acquired was crystalline which is formed from $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ phase of 150 to 200 nm of multiple and Ga_2O_3 phase of the 150 to 200 nm of multiple by analysis which is similar to Working Example 1, each crystal phase dispersed to uniform in fiber and it understood that it exists. In addition, result of doing tensile test of this fiber in sameway as Working Example 1 is shown in Table 1.

[0032] Comparative Example 1

In starting material proportion former 62 and the latter were designated as 38 with mole ratio making use of $\alpha\text{-Al}_2\text{O}_3$ powder and the ZrO_2 powder, in addition other than designating perimeter velocity of roll as the 0.5 m/sec, continuous fiber was acquired with method which is similar to the Working Example fiber which is acquired was formed from ZrO_2 phase of the 100 to 1500 nm of plural and Al_2O_3 phase of 100 to 1000 nm of plural by the analysis which is similar to Working Example 1, i

JP 00045128A Machine Translation

つまり、この繊維の組織は不均一であることがわかった。
また、この繊維の引張試験を実施例1と同様にして行
った結果を表1に示す。

understood that relatively coarse, large crystal phase from
contacting portion of roll grows in the radiating wires. In other
words, as for weave of this fiber it understood that it is a
nonuniform. In addition, result of doing tensile test of this fiber
in sameway as Working Example 1 is shown in Table 1.

【0033】

[0033]

【表1】

[Table 1]

	原料組成	ロール 周速度 (m/s)	加熱延 縮率 (%)	平均 直径 (μm)	引張強度 (GPa)		
					室温	1000℃	1200℃
実施例1	Al ₂ O ₃ /Br ₂ O ₃	2	1400	14	2.20	2.23	2.17
実施例2	Al ₂ O ₃ /Yb ₂ O ₃	2	1400	13	2.13	2.15	2.11
実施例3	Al ₂ O ₃ /Dy ₂ O ₃	2	1400	15	2.11	2.20	2.15
実施例4	Al ₂ O ₃ /Y ₂ O ₃	2	1400	14	1.61	1.65	1.61
実施例5	Al ₂ O ₃ /Cd ₂ O ₃	2	1300	11	2.01	1.98	1.85
実施例6	Al ₂ O ₃ /Sm ₂ O ₃	2	1300	12	1.89	1.89	1.83
実施例7	Al ₂ O ₃ /La ₂ O ₃	1	1300	9	1.82	1.72	1.68
実施例8	Cr ₂ O ₃ /Br ₂ O ₃	2	1300	13	1.97	1.77	1.58
実施例9	Cr ₂ O ₃ /Gd ₂ O ₃	2	1300	13	1.75	1.69	1.53
実施例10	Ga ₂ O ₃ /Gd ₂ O ₃	2	1300	15	1.69	1.67	1.51
比較例1	Al ₂ O ₃ /ZrO ₂	0.5	1300	14	0.68	0.71	0.33

【0034】

[0034]

【発明の効果】本発明によれば、高温における耐酸化性
が良好な酸化物であり、室温から高温までの引張強度が
大きく、断熱材、フィルタ材又はプラスチック、金属、
セラミックス、コンクリート等の強化材等その用途に応
じて好適に使用することができる無機繊維が提供され
る。

[Effects of the Invention] According to this invention, it is a o
xide where oxidation resistance in high temperature
issatisfactory, tensile strength to high temperature is large from
room temperature, in addition inorganic fiber which such as
insulation can be used for ideal in the broad application, filter
or plastic, metal, ceramic and concrete or other
reinforcement is offered.

【図面の簡単な説明】

[Brief Explanation of the Drawing(s)]

【図1】図1は、本発明の無機繊維の中間繊維の製造に
用いる回転ロールの形状の一例を示す図面である。

[Figure 1] Figure 1 is drawing which shows one example of geo
etry of roll which is used for production of intermediate filament
of inorganic fiber of the this invention.

【図2】図2は、本発明の無機繊維の中間繊維の製造に
用いる装置の機構の一例を示す図面である。

[Figure 2] Figure 2 is drawing which shows one example of me
anism of equipment which is used for production of intermediate
filament of inorganic fiber of the this invention.

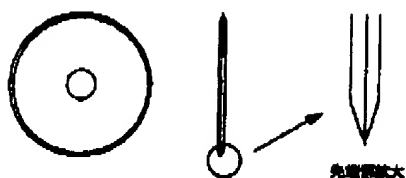
JP 00045128A Machine Translation

【符号の説明】

- 1...W電極
2...Cu製坩堝
3...アーク
4...溶融液
5...ロール
6...中間繊維

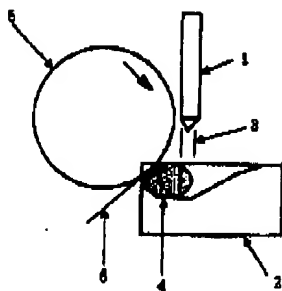
【図1】

図 1



【図2】

図 2



[Explanation of Reference Signs in Drawings]

- 1...W electrode
2... Cu make crucible
3... arc
4... molten liquid
5... roll
6... intermediate filament

[Figure 1]

[Figure 2]

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.